Enantiopure, Octadentate Ligands as Sensitizers for Europium and Terbium Circularly Polarized Luminescence in Aqueous Solution

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Abstract

Tb and Eu complexes of enantiopure ligands with a new modular design show strong overall luminescence and CPL activity in aqueous solution.

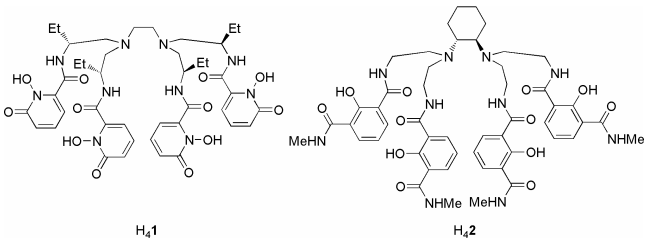
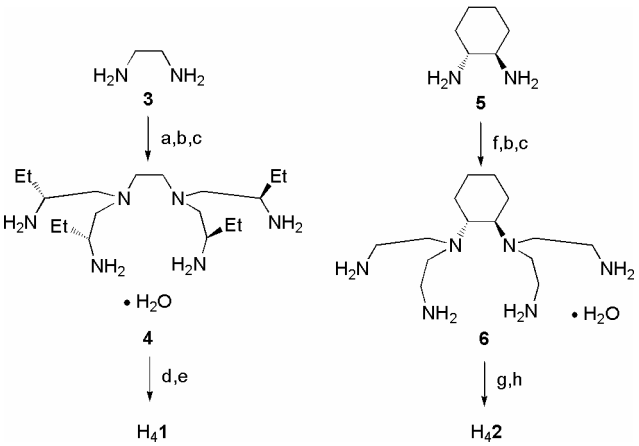


Figure 1. Enantiopure, octadentate ligands.



Scheme 1. Synthesis of ligands H$_4$**1** and H$_4$**2**.

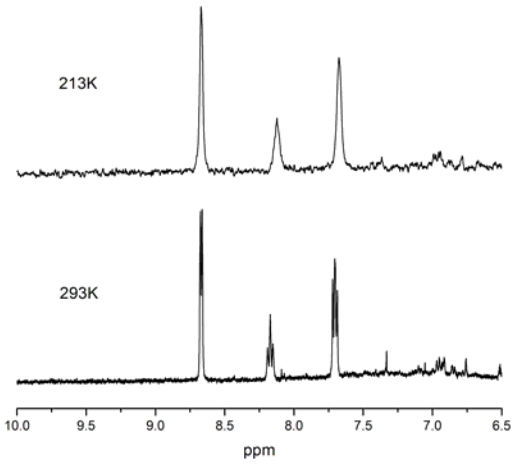


Figure 2. Aromatic region of the ^{1}H-NMR spectra (500 MHz) of a saturated solution of [Eu(H**1**)(H_2O)] in CD_3OD at 293K (bottom) and 213K (top).

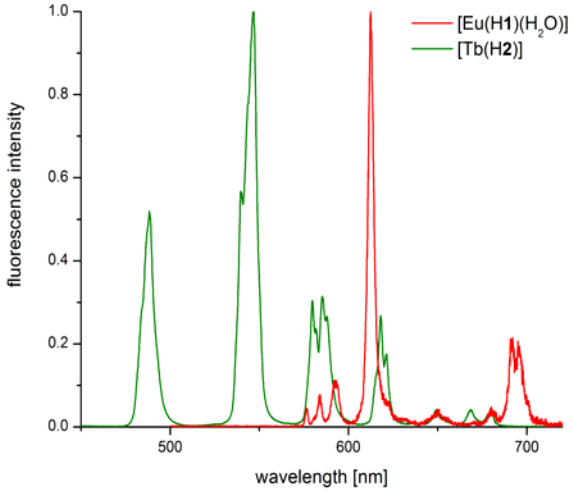


Figure 3. Normalized steady-state emission spectra (λ_{exc} = 340 nm, ca. 10^{-5} M in 0.1 M Tris buffer, pH 7.4).

Table 1. Photophysical properties of the lanthanide complexes (ca. 10^{-5} M in 0.1 M Tris buffer, pH 7.4).

Complex	λ_{max}, [nm] (ε, [$M^{-1}cm^{-1}$])	λ_{exc}, [nm]	Quantum yield Φ[a]	lifetime τ, [ms][b]	q
[Eu(H**1**)(H_2O)]	341 (19 000[c])	340	0.077	0.48 (0.88)	0.84
[Tb(H**2**)]	339 (28 200)	340	0.57	2.28 (2.59)	-0.04

[a] Determined relative to quinine sulfate (Φ=0.546) in 0.5 M sulfuric acid as standard; [b] in H_2O (in D_2O); [c] sat. solution, estimated ε.

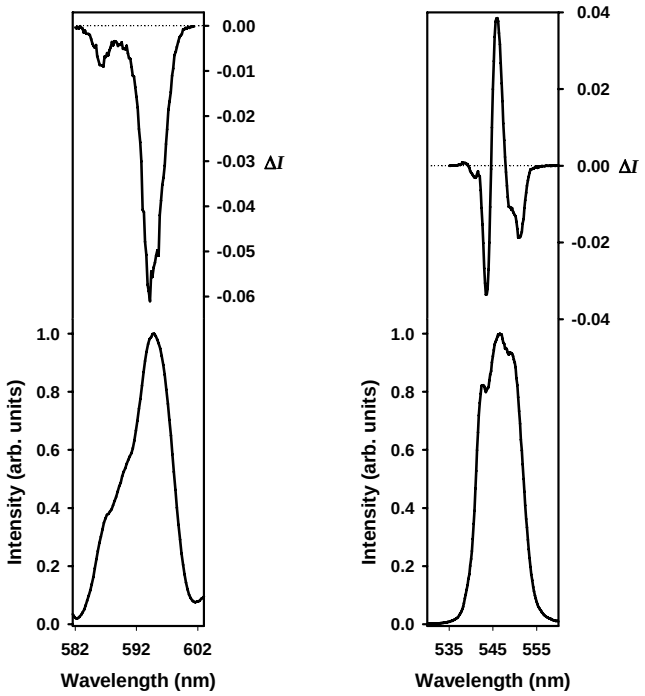


Figure 4. Circularly polarized luminescence (upper curves) and total luminescence (lower curves) spectra of the $^5D_0 \rightarrow {}^7F_1$ transition of [Eu(H**1**)(H2O)] (left) and $^5D_4 \rightarrow {}^7F_5$ transition of [Tb(H**2**)] (right) in saturated aqueous solutions at pH 7.4 (0.1 M Tris buffer) and 295 K, upon excitation at 360 and 350 nm, respectively.

Table 2. CPL results for lanthanide complexes (saturated aqueous solutions in 0.1 M Tris buffer, pH 7.4).

Complex	Electronic transition	λ [nm]	g_{lum}
[Eu(H**1**)(H_2O)]	$^5D_0 \rightarrow {}^7F_1$	586.6	-0.046
		594.2	-0.12
[Tb(H**2**)]	$^5D_4 \rightarrow {}^7F_5$	543.6	-0.083
		545.8	+0.078
		551.0	-0.051